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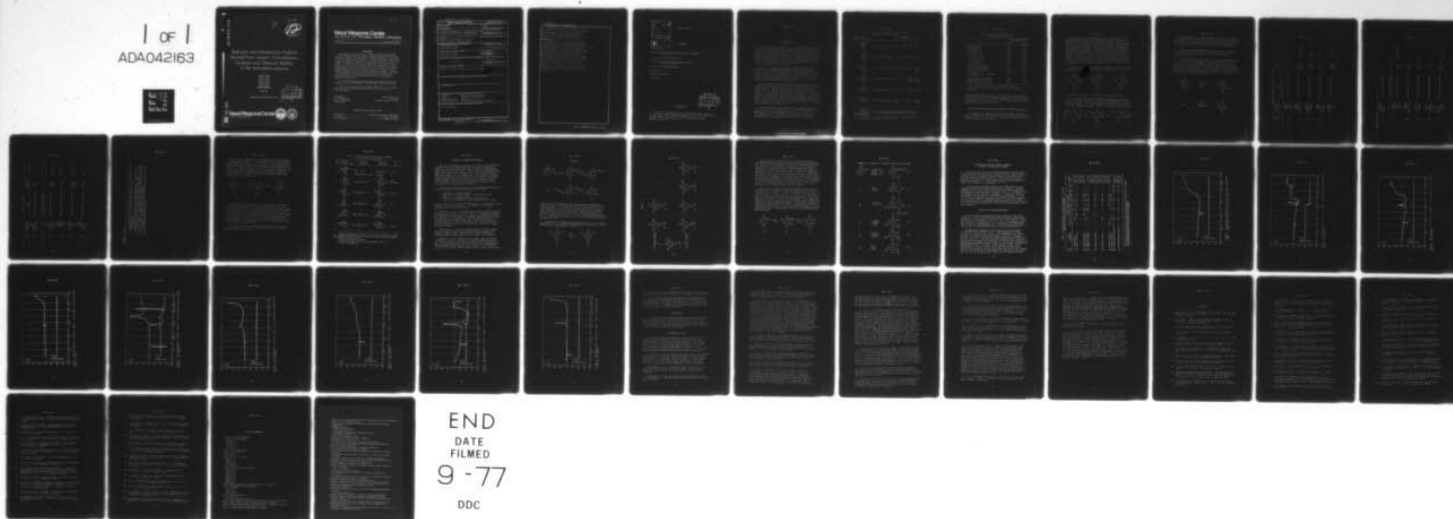
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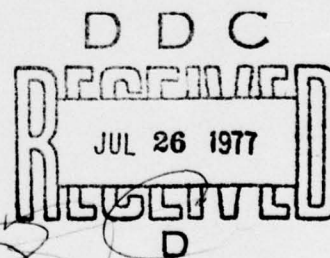
NWC TP 5933

Reduction and Ammonolysis Products
Derived From Isomeric Trinitrotoluenes.
Synthesis and Chemical Stability
of the Aminodinitrotoluenes

by
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JUNE 1977

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F. H. M. Kinley, Capt., USN Commander

R. M. Hillyer Technical Director (Acting)

FOREWORD

The safety of Navy explosives containing 2,4,6-trinitrotoluene (α -TNT) and ammonium nitrate (Minol, Pamatex, Amatex) depends on the potential chemical reactions between component ingredients. One method of value in studying this problem is to examine reactions between pure samples of individual components of the explosive mixture. Thus, trace amounts of impurities (such as α -TNT isomers) can be evaluated with respect to their potential reaction with other ingredients. In the present study the reaction between α -TNT and its isomers with ammonia has been examined and certain chemical reactions defined. Selected aminodinitrotoluene reaction products derived from isomeric trinitrotoluenes have been synthesized and their chemical stability evaluated. It is concluded that the aminodinitrotoluenes are rather stable compounds (more stable than α -TNT itself) and do not represent a potential storage hazard.

The work described was performed under NWC Independent Research funds, task area number ZR01301, during calendar years 1975 and 1976.

This report was reviewed for technical accuracy by T. B. Joyner and C. D. Lind of the Naval Weapons Center and E. E. Gilbert of Picatinny Arsenal.

Released by
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Research Department
30 June 1977

Under authority of
R. M. HILLYER
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NWC Technical Publication 5933

Published by Technical Information Department
Collation Cover, 21 leaves
First printing 155 unnumbered copies

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SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM
1. REPORT NUMBER NWC-TP-5933	2. GOVT ACCESSION NO.	3. RECIPIENT'S CATALOG NUMBER (9)
4. TITLE (and Subtitle) REDUCTION AND AMMONOLYSIS PRODUCTS DERIVED FROM ISOMERIC TRINITROTOLUENES. SYNTHESIS AND CHEM- ICAL STABILITY OF THE AMINODINITROTOLUENES.	5. TYPE OF REPORT & PERIOD COVERED A Research Report. 1975-1976.	6. PERFORMING ORG. REPORT NUMBER
7. AUTHOR(s) Arnold T. Nielsen, Ronald L. Atkins Ronald A. Henry, Donald W. Moore William P. Norris, Albert H. Lepie	8. CONTRACT OR GRANT NUMBER(s)	
9. PERFORMING ORGANIZATION NAME AND ADDRESS Naval Weapons Center China Lake, CA 93555	10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS Task Area Number ZR01301	
11. CONTROLLING OFFICE NAME AND ADDRESS Naval Weapons Center China Lake, CA 93555	12. REPORT DATE June 1977	13. NUMBER OF PAGES 40
14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office) (12) 42p.	15. SECURITY CLASS. (of this report) UNCLASSIFIED	15a. DECLASSIFICATION/DOWNGRADING SCHEDULE
16. DISTRIBUTION STATEMENT (of this Report) Approved for public release; distribution unlimited.		
17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)		
18. SUPPLEMENTARY NOTES		
19. KEY WORDS (Continue on reverse side if necessary and identify by block number) Explosives Differential Thermal Analysis Safety TNT Reactions with Ammonia Aminodinitrotoluenes Reduction Impact Sensitivity Nuclear Magnetic Resonance Spectroscopy		
20. ABSTRACT (Continue on reverse side if necessary and identify by block number) See back of form.		

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(U) *Reduction and Ammonolysis Products Derived from Isomeric Trinitrotoluenes. Synthesis and Chemical Stability of the Aminodinitrotoluenes*, by Arnold T. Nielsen, Ronald A. Henry, William P. Norris, Ronald L. Atkins, Donald W. Moore, and Albert H. Lepie. China Lake, Calif., Naval Weapons Center, June 1977. 40 pp. (NWC TP 5933, publication UNCLASSIFIED.)

(U) The reaction of ammonia with the six isomeric trinitrotoluenes has been examined. Syntheses of eight aminodinitrotoluenes, including all derived by ammonolysis of the five unsymmetrical trinitrotoluenes, and reduction of 2,4,6-trinitrotoluene (α -TNT), are described. Synthesis of the sixteenth, and only previously unreported aminodinitrotoluene isomer, 3-amino-2,5-dinitrotoluene, has been achieved. Nuclear magnetic resonance spectra support the structure assignments. Impact sensitivities and decomposition temperatures (determined by differential thermal analysis) were determined for all eight aminodinitrotoluenes described in this report. All compounds were found to be quite stable, more stable than α -TNT itself. It is concluded that potential formation of aminodinitrotoluenes by reaction of ammonia with impurities in military grade TNT does not constitute a safety hazard.

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ACKNOWLEDGMENT

The authors are indebted to E. E. Gilbert of Picatinny Arsenal and W. T. Bolleter of Radford Army Ammunition Plant for helpful discussions and suggestions. They also wish to thank Col. John R. C. Roop, Commander, Radford AAP for assistance in securing the TNT data summarized in Table 2.



INTRODUCTION

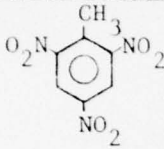
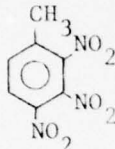
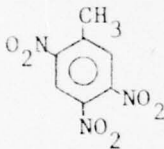
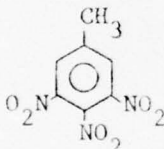
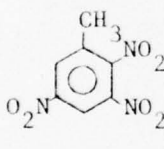
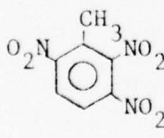
The safety of military ordnance, to an important degree, is related to the potential chemical reactions between component ingredients. The stability of certain explosives containing 2,4,6-trinitrotoluene (α -TNT) and ammonium nitrate (Minol, Pamatex, Amatex) depends on the extent of reaction of the TNT with the ammonium nitrate component. Other questions of importance are the related reaction of TNT with ammonia itself, the identification of products formed, and the stability of these products. Storage life and the safety of munitions could be affected by such reactions. The compatibility of explosive ingredients on storage must be considered a matter of major importance.

The present study addresses an important question concerning the compatibility of explosives containing TNT and ammonia derivatives. That is, what are the explosive properties of the principal ammonolysis products of the isomeric trinitrotoluenes -- the aminodinitrotoluenes (dinitrotoluidines)? The answer has been found by examination of selected isomeric aminodinitrotoluenes: these materials are actually quite stable (more stable than α -TNT itself) and it is concluded that they do not represent a potential storage hazard.

Crude TNT prepared by the batch process is a mixture containing principally α -TNT (1, 93 to 95%) and small amounts of isomeric trinitrotoluenes and other impurities (Table 1).¹⁻⁵ (References 1 through 16 are cited in Table 1.) All six of the isomeric trinitrotoluenes may be present. The principal TNT impurity is the γ -isomer, 2,4,5-trinitrotoluene (3). Minor amounts of certain dinitrotoluenes, trinitrobenzenes, trinitrocresols, and other compounds may also be present.⁵ After purification by the Sellite process (sodium sulfite treatment) most of the unsymmetrical trinitrotoluenes are removed as water-soluble sulfonate salts. Military grades of α -TNT usually freeze above 80°C and contain less than 2% of impurities, mainly TNT isomers. Crude TNT freezes at ca. 75 to 76°C and pure α -TNT freezes at 80.75 \pm 0.05°C.

At the present time α -TNT is prepared by a continuous process at the Army Ammunition Plant. An analysis of the impurities in the crude and finished products is summarized in Table 2.¹⁷⁻²⁰ The amounts of TNT isomers present in crude material prepared by either batch or continuous process are very similar (compare Tables 1 and 2). The finished product contains materials absent in the crude including

TABLE 1. Isomeric Trinitrotoluenes Present in Crude TNT Prepared by a Batch Process.

Cpd. no.	Structural formula	Form	Name	m.p. °C	Ignition temp, °C ^a	% ^b	Ref. ^c
1		α	2,4,6-Trinitrotoluene	80.8	290	93-95	1-6
2		β	2,3,4-Trinitrotoluene	112	302	1.4-1.6	1-10
3		γ	2,4,5-Trinitrotoluene	104-104.5	291	2.6-2.7	1-6, 9,11, 12
4		δ	3,4,5-Trinitrotoluene	137.5	313	0.002- 0.006	1-3, 5,13, 14
5		ε	2,3,5-Trinitrotoluene	97.5	332	0.01- 0.04	1-3, 5, 15
6		η	2,3,6-Trinitrotoluene	111.5- 112.5	335	0.15- 0.4	1-5, 8,16

^a Data of Ref. 5.^b Data of Ref. 2-4. Other impurities include dinitrotoluenes, trinitrobenzenes, di- and trinitrocresols, trinitrobenzoic acids, and tetranitromethane.^c References refer to data in this Table and to publications on synthesis and structure cited in this report.

TABLE 2. Impurities Present in TNT Prepared by a Continuous Process.^a

Compound	Approximate maximum nominal concentration (%) ^b	
	Crude	Finished
2,6-Dinitrotoluene	0.25	0.25
2,4-Dinitrotoluene	0.50	0.50
2,3-Dinitrotoluene	0.05	0.05
2,5-Dinitrotoluene	0.10	0.10
3,4-Dinitrotoluene	0.10	0.10
3,5-Dinitrotoluene	0.01	0.01
2,4,5-Trinitrotoluene	2.50	0.30
2,3,4-Trinitrotoluene	1.75	0.20
2,3,6-Trinitrotoluene	0.50	0.05
2,3,5-Trinitrotoluene	0.05	0.05
1,3-Dinitrobenzene	0.02	0.02
1,3,5-Trinitrobenzene	0.15	0.10
2,4,6-Trinitrobenzyl alcohol	0.25	0.25
2,4,6-Trinitrobenzaldehyde	0.25	0.25
2,4,6-Trinitrobenzoic acid	0.50	0.05
α -Nitro-2,4,6-trinitrotoluene	0.10	0.10
Tetranitromethane	0.10	none
2,2'-Dicarboxy-3,3',5,5'-tetranitro-azoxybenzene	0.35	0.05
2,2',4,4',6,6'-Hexanitrobibenzyl	none	0.40
3-Methyl-2',4,4',6,6'-pentanitrodiphenylmethane	none	0.40
3,3',5,5'-Tetranitroazoxybenzene	none	0.01

^a Data from Radford Army Ammunition Plant, Radford, Virginia.

^b Concentrations listed are the maximum possible. Actual values will be much lower.

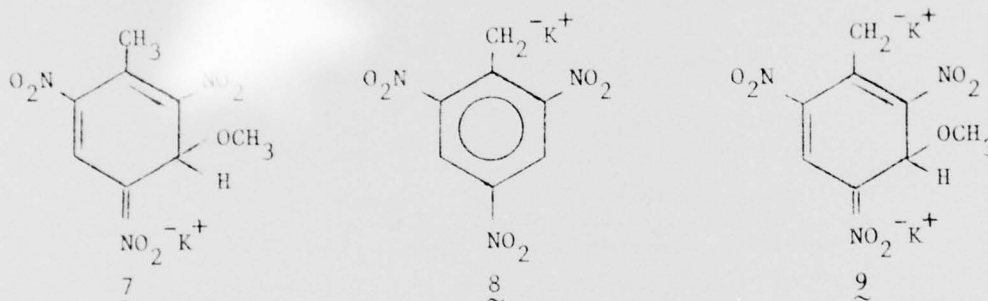
2,2',4,4',6,6'-hexanitrobibenzyl, 3-methyl-2',4,4',6,6'-pentanitrodiphenylmethane and 3,3',5,5'-tetranitroazoxybenzene. These compounds arise from the Sellite process. The finished product also may contain small amounts of the impurities found in the crude (approximate maximum concentrations are listed in Table 2).

REACTION OF TRINITROTOLUENES WITH AMMONIA AND AMMONIA DERIVATIVES

The reaction of α -TNT and its isomers with ammonia and ammonia derivatives has been studied by others. Although pure ammonium nitrate shows no reaction with pure α -TNT, the presence of bases permits release of ammonia which can then react.²¹

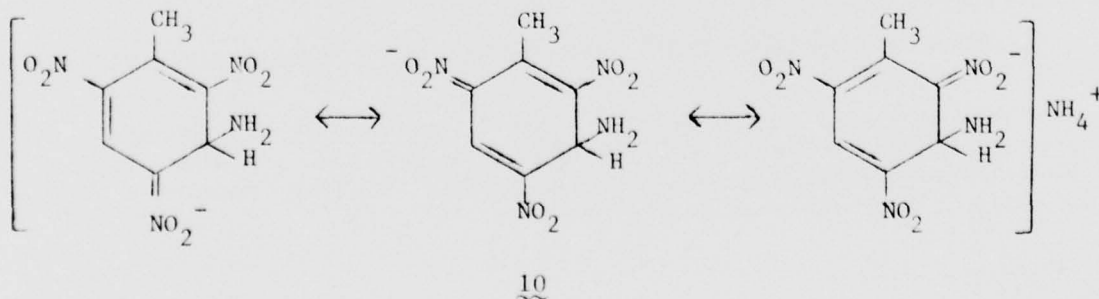
Lang and Boileau,²¹ Korczinski,²² and Giua and Reggiani²³ noted that the reaction of α -TNT with anhydrous ammonia gave an unstable addition product containing two molecules of ammonia. The material was described as a bright red crystalline material which decomposed at 180 to 200°C to liberate ammonia. No structural formula was assigned. In air the material turned dark. When treated with water it decomposed to yield ammonium nitrite and unidentified noncrystalline material (not recovered α -TNT). One sample of the hydrolysate gave an analysis corresponding to an aminodinitrotoluene (found: %N, 21.50; calcd. for $C_7H_7N_3O_4$: %N, 21.32).²¹ Other samples gave similar analyses, but the analytical results were variable. In the present study an ethanolic solution of α -TNT was treated with excess gaseous ammonia at 25-40°C (90 minutes) to yield a deep red solution. Removal of the solvent gave a red solid, which when treated with water gave a dark amorphous solid, unidentified.

The reaction of α -TNT with methoxide ion leads to rapid formation of a brown-colored Meisenheimer adduct (7), followed by a slower formation of purple carbanion 8.²⁴



In more concentrated base a reddish-colored dianion (9) is formed.²⁴

By analogy with the methoxide addition, the addition of two molecules of the weaker base, ammonia, to α -TNT would be expected to yield adduct salt 10 and correspond to the red crystalline material isolated by previous workers.²¹⁻²³ Loss of ammonium nitrite from 10 could yield one or more aminodinitrotoluenes. The reaction should be reinvestigated.



Aminodinitrotoluenes 2-amino-4,6-dinitrotoluene (15) and 4-amino-2,6-dinitrotoluene (25) are formed by reduction of α -TNT with ammonium polysulfide.²⁵⁻³⁸ This reaction has been reinvestigated in the present work and new results discussed below. Properties of aminodinitrotoluenes are summarized in Table 3. (This table contains, among others, ref. 25-52.)

The reaction of the unsymmetrical trinitrotoluenes with ammonia in alcohol solvents leads to the aminodinitrotoluenes^{6,8,9,11-16,45} often in high yield.¹²⁻⁴⁵ Amines react to yield N-substituted aminodinitrotoluenes.⁵³⁻⁵⁵

These ammonia reactions are similar to that of sodium sulfite with α -TNT isomers (Sellite process) in that a displacement of one of the nitro groups occurs. For example, reaction of 3 (γ -TNT) with sodium sulfite leads to sodium 4,6-dinitro-3-methylbenzenesulfonate (27) with elimination of sodium nitrite.⁵ Similarly, reaction of 3 with ammonia leads to 5-amino-2,4-dinitrotoluene (21) with loss of ammonium nitrite. These reactions do not proceed beyond the formation of the dinitrotoluene derivatives (no diaminonitrotoluenes are formed). Also, sodium sulfite does not react with dinitrotoluenes.

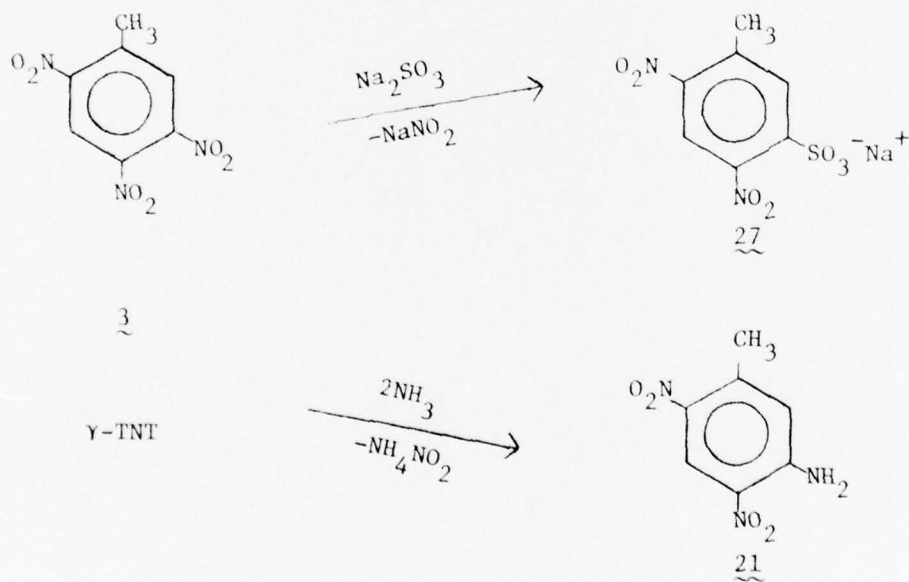


TABLE 3. Isomeric Aminodinitrotoluenes.

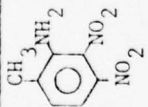
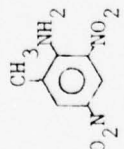
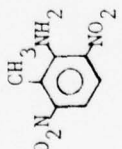
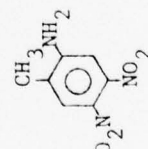
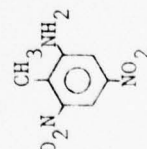
Cpd. no.	Structural formula	Name	m.p. °C ^d (dec., °C) ^{i, c}	Ref. ^d
Dinitro-ortho Toluidines				
11		2-Amino-3,4-dinitrotoluene	131-131.5	1, 7, 39
12		2-Amino-3,5-dinitrotoluene	215-217 217-218 (320)	^b 1, 14, 35, 40-42 ^{b, c}
13		2-Amino-3,6-dinitrotoluene	148-151 151 (300)	^b 1, 16, 41 ^{b, c}
14		2-Amino-4,5-dinitrotoluene	191-191.5	7, 39
15		2-Amino-4,6-dinitrotoluene	175-176 173-174 (307)	^b 26, 27, 33, 35, 37, 43, 44 ^{b, c}

TABLE 3. (Contd.)

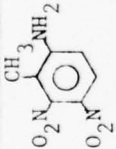
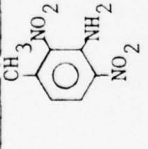
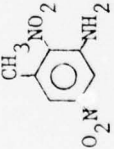
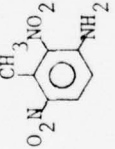
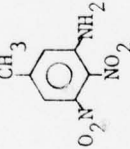
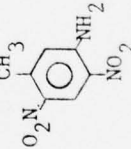
16		6-Amino-2,3-dinitrotoluene	216	8, 37
Dinitro-meta Toluidines				
17		3-Amino-2,4-dinitrotoluene	94 (280)	6, 9, 11, 12, 45, 46 b, c
18		3-Amino-2,5-dinitrotoluene	127-128 (350)	b b, c
19		3-Amino-2,6-dinitrotoluene	134	16, 47
20		3-Amino-4,5-dinitrotoluene	141	48
21		5-Amino-2,4-dinitrotoluene	197-199 196, 5-197.5 (320)	b 6, 9, 11, 42, 46, 49 b, c

TABLE 3. (Contd.)

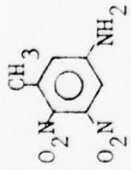
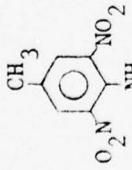
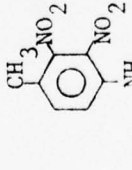
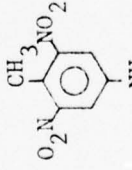
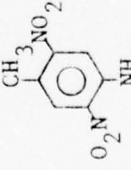
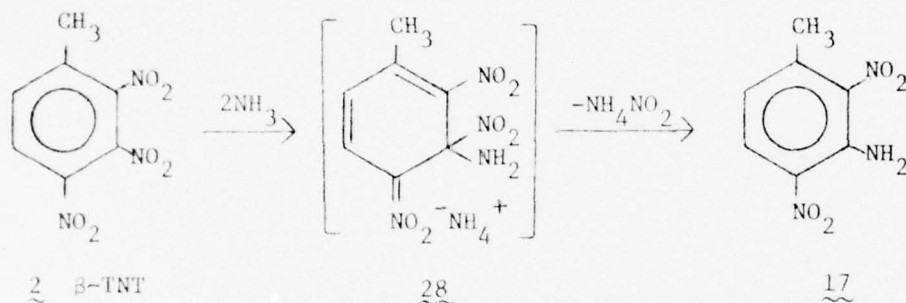
Cpd. no.	Structural formula	Name	m.p. °C ^a (dec., °C) <i>b, c</i>	Ref. ^d
22 ~		5-Amino-2,3-dinitrotoluene	165	48
Dinitro-para Toluidines				
23 ~		4-Amino-3,5-dinitrotoluene	176-177 172 (250) ^e	<i>b</i> 1,42,48,50,51 <i>b, c</i>
24 ~		4-Amino-2,3-dinitrotoluene	125.5-126	10, 50, 52
25 ~		4-Amino-2,6-dinitrotoluene	171-172 171-172 (325)	<i>b</i> 8,26-38,43 <i>b, c</i>
26 ~		4-Amino-2,5-dinitrotoluene	190-191	10, 50

TABLE 3. (Contd.)

- ^a In addition to the first-listed melting point of the present work, only the highest melting point reported by other workers is listed.
- ^b Present work.
- ^c Decomposition temperatures are exothermic maxima or temperatures of initiation obtained by differential thermal analysis (Fig. 1-8).
- ^d References refer to the highest melting points reported and other work cited in this report. Numerous additional references describing preparations of various aminodinitrotoluidines have not been listed.
- ^e Initiation of exotherm occurs at this temperature; no sudden exotherm or gas evolution was noted (see Fig. 7).

The reaction of ammonia with the unsymmetrical trinitrotoluenes is believed to involve formation of an intermediate sigma complex similar to a Meisenheimer complex.^{5,11,56,57} Ammonia reacts as a nucleophile attacking the ring carbon atom ortho and para to ring-substituted nitro groups. For example, reaction of β -TNT (2) with ammonia will result in attack at the 3-position leading to nitronate salt 28. Subsequent loss of nitrite ion from C-3 produces the isolated product, 3-amino-2,4-dinitrotoluene (17). Ammonium nitronate salts such as 10 and 28 are unstable, sensitive compounds, and should be considered undesirable ingredients of stored munitions.



The position of ammonia attack on the isomeric trinitrotoluenes to yield aminodinitrotoluenes has been established (Table 3). Attack occurs preferentially (with resulting exchange of nitro by amino) and at different rates. In order of ease of aromatic ring nitro-amino exchange are: (1) nitro ortho to two nitro groups; (2) nitro ortho to a nitro group and a methyl; and (3) nitro ortho and para to nitro groups. Nitro groups meta to a nitro group are not attacked by ammonia to yield amino-dinitrotoluenes. Since α -TNT is the only trinitrotoluene having all nitro groups meta to each other, it is the only one which does not directly produce a dinitrotoluidine by reaction with ammonia under known conditions (see discussion above).

All of the possible aminodinitrotoluenes derived from isomeric trinitrotoluenes by ammonolysis have been synthesized in the present study. Compare Tables 3 and 4.

TABLE 4. Products Derived by Reaction of Ammonia With Isomeric Trinitrotoluenes.

Cpd. no.	Trinitro-toluene	Form	Reaction conditions	Principal product(s)	Ref.
1		α	$\text{NH}_3, -10^\circ\text{C}$ $\text{NH}_3, \text{CH}_2(\text{OCH}_3)_2, -5^\circ\text{C}$	$\text{C}_7\text{H}_{11}\text{N}_5\text{O}_6^{a,b}$ $\text{C}_7\text{H}_7\text{N}_3\text{O}_4^b$	5, 21, 22 21
2		β	$\text{NH}_3, \text{C}_2\text{H}_5\text{OH}, 78^\circ\text{C}$	 17^c	6, 9 11, 12, 45, d
3		γ	$\text{NH}_3, \text{C}_2\text{H}_5\text{OH}, 25^\circ\text{C}$	 21	6, 9, 11, d
4		δ	$\text{NH}_3, \text{C}_2\text{H}_5\text{OH}, 25^\circ\text{C}$	 23	14, d
5		ϵ	$\text{NH}_3, \text{C}_2\text{H}_5\text{OH}, 25^\circ\text{C}$	 12	14
6		ζ	$\text{NH}_3, \text{C}_2\text{H}_5\text{OH}, 78^\circ\text{C}$	 13	8, 14, 16, d

^a Product described as an adduct of α -TNT with 2 molecules of ammonia. Ammonium polysulfide reduction yields 2-amino-4,6-dinitrotoluene and 4-amino-2,6-dinitrotoluene.

^b Structure unknown (see text).

^c Product 17 formed in 90 to 95% yield (Ref. 12, 45).

^d Present investigation.

SYNTHESIS OF AMINODINITROTOLUENES

There are 16 aminodinitrotoluenes theoretically possible (Table 3). Fifteen of these were known at the time this study was initiated. Synthesis of the remaining unknown isomer, 3-amino-2,5-dinitrotoluene (18), is described in this report. A total of eight aminodinitrotoluene isomers were prepared in the present work. These included the five ammonolysis products of the unsymmetrical trinitrotoluenes (compounds 12, 13, 17, 21 and 23, Tables 3 and 4), the two derived by reduction of α -TNT (15 and 25) and 18. These materials were considered to be the isomers of major significance because of their relationship to the trinitrotoluenes. They were also selected as representative of the entire group for study of explosive behavior.

The principal methods of synthesis of the aminodinitrotoluenes may be grouped according to reaction and reactant as follows:

1. Ammonolysis of trinitrotoluenes
2. Ammonolysis of hydroxy, alkoxy or halodinitrotoluenes
3. Reduction of trinitrotoluenes
4. Nitration of mononitrotoluidines and derivatives
5. Schmidt reaction (hydrazoic acid) with dinitrotoluic acids

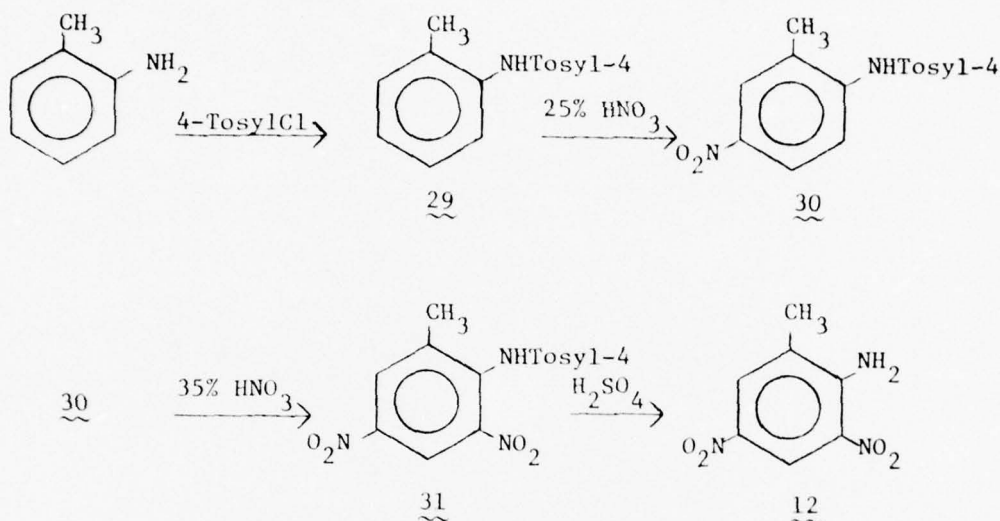
Details of most of the synthetic methods employed by others may be found in the references listed in Table 3. Discussion of the syntheses employed in the present study follows.

Reaction of β -, γ -, δ - and η -TNT (2, 3, 4 and 6, respectively) with excess ethanolic ammonia (at reflux or 25°C) gave aminodinitrotoluenes 17, 21, 23 and 13, respectively (cf. Table 4). The ammonolysis product of ϵ -TNT (2,3,5-trinitrotoluene, 5), 2-amino-3,5-dinitrotoluene (12) was synthesized by an alternate route. The *p*-toluenesulfonamide of *o*-toluidine (29) was nitrated in two steps to yield first the mono-nitro derivative 30 with 25% nitric acid, followed by nitration with 35% nitric acid to yield the dinitro derivative 31. Hydrolysis of 31 produced 12⁴⁰ (Scheme I).

The reduction of α -TNT with hydrogen sulfide in dioxane solvent (ammonia catalyst) leads to 4-amino-2,6-dinitrotoluene (25) as the principal product (99% by nuclear magnetic resonance (NMR) assay). 2-Amino-4,6-dinitrotoluene (15) is a minor product (1%) (Scheme II).

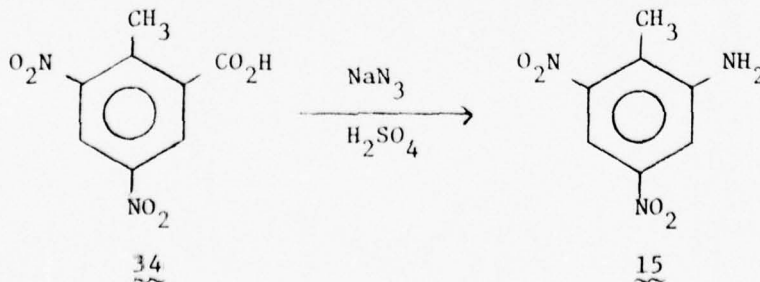
Reduction of α -TNT in ethanol solvent takes a different course (Scheme II). A mixture of products is produced containing unreacted TNT. The reduction products (ca. 50% yield total) are principally 4-amino-2,6-dinitrotoluene (25, 28% of the product) and 4-hydroxylamino-2,6-dinitrotoluene (32, 57%) obtained by reduction of the C-4 nitro group (cf. Ref. 27-38). Formed in small amounts in these reductions are

SCHEME I

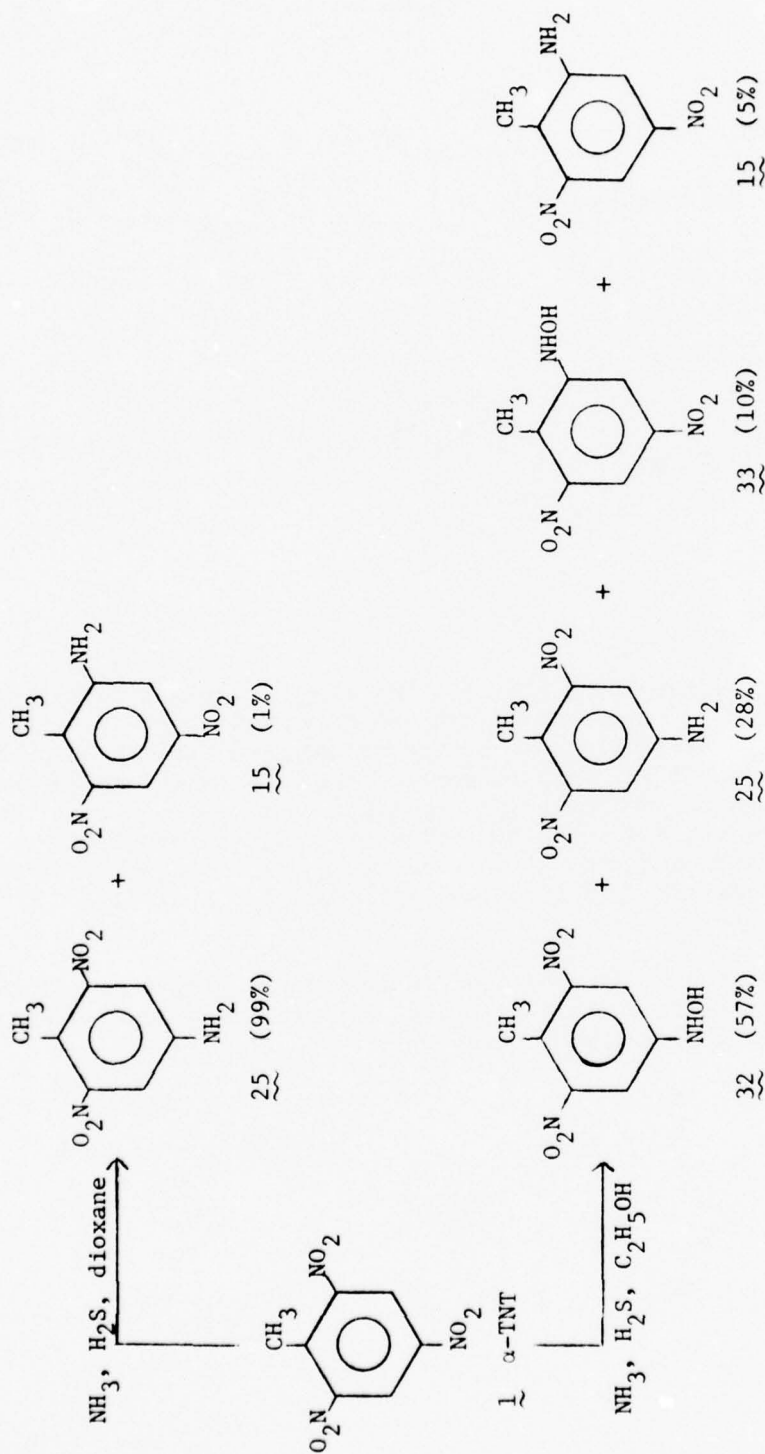


2-amino-4,6-dinitrotoluene (15, 5%) and 4,6-dinitro-2-hydroxylaminotoluene (33, 10%). Compound 33 has not previously been identified as a reduction product of TNT. Its structure and assay and those of the other components of the mixture were established by column chromatography, NMR spectra, and mass spectroscopy. A product, m.p. 155°C, obtained by hydrogen sulfide reduction of α -TNT and described as pure 15,^{33,35} has been shown by us to be a mixture containing principally 15 and the 4-hydroxylamino derivative, 32. Pure 15 is difficult to prepare by reduction of TNT.

A sample of pure 2-amino-4,6-dinitrotoluene (15, m.p. 175 to 176°C) has been prepared from 2-methyl-3,5-dinitrobenzoic acid (34) by reaction with hydrazoic acid (Schmidt reaction).^{25,43}

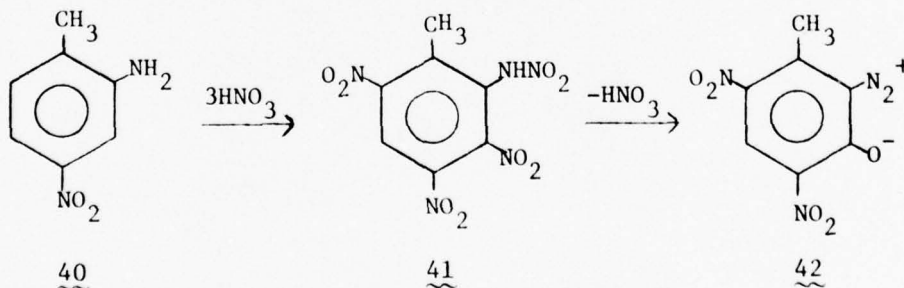


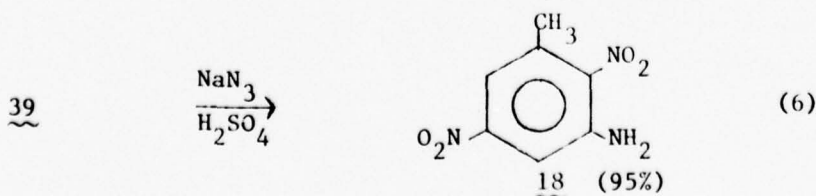
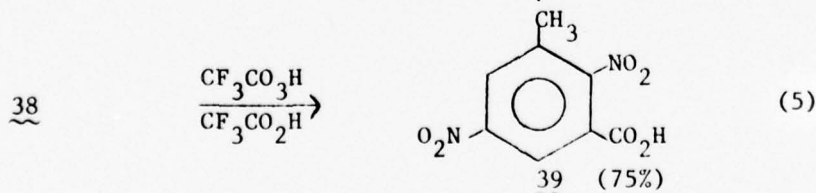
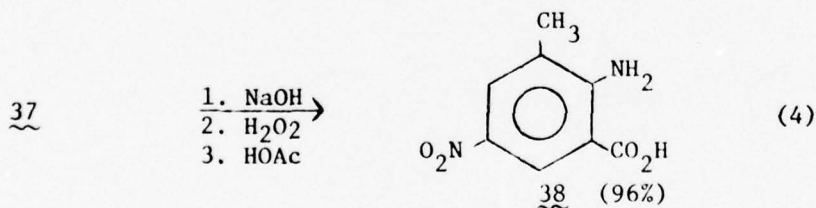
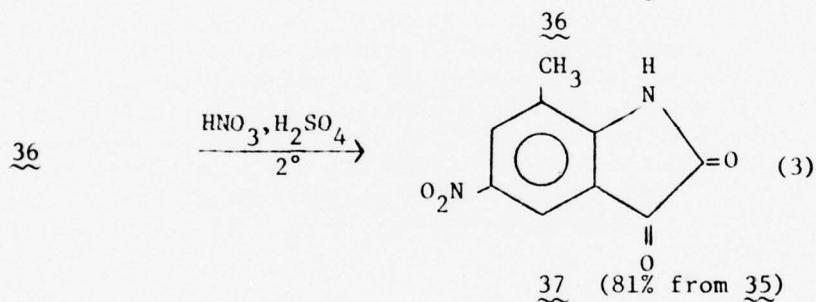
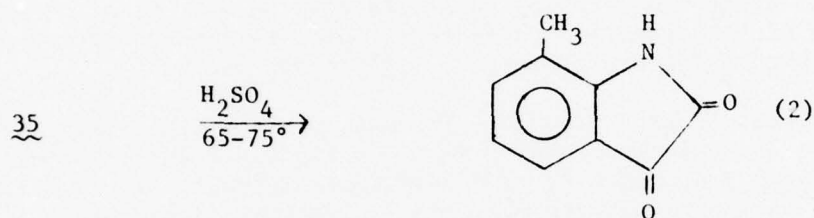
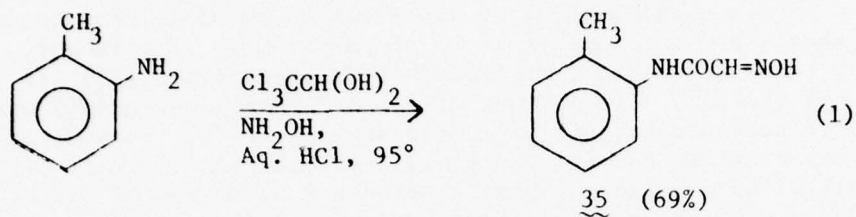
SCHEME II



One aminodinitrotoluene, 3-amino-2,5-dinitrotoluene (18), not previously described was prepared by the reactions presented in Scheme III. Most of the usual methods of synthesis of aminodinitrotoluenes, outlined above, are not applicable to preparation of this isomer. Starting with *o*-toluidine, *o*-methylisonitrosoacetanilide (35) was prepared in 69% yield.⁵⁸ Cyclization of 35 to 7-methylisatin (36) was conducted in concentrated sulfuric acid at 65 to 75°C. Without isolation, 36 was nitrated directly to yield 7-methyl-5-nitro-isatin (37) in 81% overall yield from 35. Saponification and oxidation of 37 led to 2-amino-3-methyl-5-nitrobenzoic acid 38 in 96% yield. Emmons oxidation⁵⁹ of 38 with peroxytrifluoroacetic acid in trifluoroacetic acid solvent led to 2,5-dinitro-3-methylbenzoic acid (39) in 75% yield. Treatment of this acid with hydrazoic acid in the Schmidt reaction produced the desired 3-amino-2,5-dinitrotoluene (18) in 95% yield.

The reaction of 2-methyl-5-nitroaniline (40) with fuming nitric acid (90%) has been reported by Kapil to produce 2-amino-4,6-dinitrotoluene (15), m.p. 160°C.⁶⁰ (We have found authentic 15 to melt at 175 to 176°C; Sitzman²⁵ reports m.p. 173 to 174°C.) In our hands, Kapil's procedure gave a very sensitive explosive compound, m.p. 152 to 154°C (with rapid decomposition followed by an explosion with a flash; impact sensitivity less than 10 cm with a 2.5 kg weight). Based on NMR, mass spectra and infrared spectra, the material is tentatively identified as 2-diazo-4,6-dinitro-3-methylphenol (42). Glowiak has prepared 4-diazo-2,6-dinitro-3-methylphenol.⁶¹⁻⁶³ From the study of Scilly and co-workers the reaction may be described as proceeding through a nitramine intermediate (41).⁶⁴ The mechanism of the 41 → 42 conversion has not been elucidated.



SCHEME III. Synthesis of 3-Amino-2,5-dinitrotoluene (18).

STRUCTURE AND NUCLEAR MAGNETIC RESONANCE
SPECTRA OF AMINODINITROTOLUENES

The structure of each of the isomeric aminodinitrotoluenes (Table 3) has been carefully established by several methods. These include the synthetic route, conversion to known compounds, chemical behavior and physical properties, including spectra. Much of the work on determination of the position of substituents is described in the papers of Körner and Contardi,^{13,15,16} Brady and co-workers,^{7,8,34,46,48,53,54} Giua,^{11,23,55} Cohen³⁰⁻³² and Robinson.^{10,45}

In the present study high resolution proton NMR spectra of the eight aminodinitrotoluenes prepared have been determined. Their NMR parameters and those of α -TNT, 4-hydroxylamino-2,6-dinitrotoluene and 2-hydroxylamino-4,6-dinitrotoluene are given in Table 5. The spectra are in agreement with the structural assignments. For example, expected ring proton coupling values are observed for meta hydrogens ($J = 2.84$ and 2.48 Hz for compounds 12 and 18, respectively) and ortho hydrogens ($J = 9.11$ and 8.82 Hz for compounds 13 and 17, respectively). Weak coupling between the ring hydrogens and the methyl group is also observed ($J < 1$ Hz); coupling constants are strongest for ortho and weakest for meta hydrogens.

STABILITY OF AMINODINITROTOLUENES

Of the 16 possible aminodinitrotoluenes, eight have been synthesized in the present work, including all those derived by ammonolysis of unsymmetrical trinitrotoluenes and reduction of α -TNT (Table 3). Physical properties are summarized in Table 3. All of the aminodinitrotoluenes are stable, crystalline solids with melting points ranging from 94°C (3-amino-2,4-dinitrotoluene, 17) to 217 - 218°C (2-amino-3,5-dinitrotoluene, 12); the remainder have melting points between 125 - 200°C .

Decomposition temperatures (first exotherm) were established by differential thermal analysis (DTA) for eight aminodinitrotoluenes (12, 13, 15, 17, 18, 21, 23, and 25). These temperatures are listed in Table 3 and the DTA curves are presented in Figures 1 through 8. The curve for α -TNT is included for comparison (exothermic decomposition at 320°C , Figure 9). With the exception of compounds 17 and 23 which exhibit initial decomposition temperatures of 280 and 250°C , respectively, the aminodinitrotoluenes examined reveal initial exothermic decomposition between 300 to 325°C . All may be considered quite stable to heat. Those having the lowest stability (17 and 23) have an amino group between two nitro groups. Since these isomers are the only ones showing this structural feature, the eight isomers not examined in the present work (11, 14, 16, 19, 20, 22, 24, and 26) would be expected to have

TABLE 5. Proton Nuclear Magnetic Resonance Parameters for Selected Aminodinitrotoluenes and Related Compounds.

Cpd. no.	Toluene substitution	Chemical shifts, δ , ppm ^{a,b}							J-values, Hz
		H-2	H-3	H-4	H-5	H-6	CH ₃	NH ₂ ^c	
1	2,4,6-Trinitro-	9.01	9.01	2.69	J _{3Me} = 0.43
12	2-Amino-3,5-dinitro-	8.86	8.09	2.45	7.72	J ₄₆ = 2.84 J _{4Me} = 0.56 J _{6Me} = 0.88
13	2-Amino-3,6-dinitro-	8.17	7.02	2.31	7.29	J ₄₅ = 9.11
15	2-Amino-4,6-dinitro-	7.82	7.82	2.31	5.91
17	3-Amino-2,4-dinitro-	8.24	6.80	2.41	7.33	J ₅₆ = 8.82 J _{5Me} = 0.24 J _{6Me} = 0.55
18	3-Amino-2,5-dinitro-	7.73	7.37	2.46	6.22	J ₄₆ = 2.48 J _{4Me} = 0.58 J _{6Me} = 0.73
21	5-Amino-2,4-dinitro-	8.89	7.03	2.58	7.69	J ₃₆ = 0.30 J _{3Me} = 0.22 J _{6Me} = 0.84
23	4-Amino-3,5-dinitro-	8.42	8.42	2.41	8.35	J _{2Me} = 0.80
25	4-Amino-2,6-dinitro-	7.40	7.40	2.30	5.72
32	4-hydroxylamino-2,4-dinitro-	7.66	7.66	2.39	J _{NH-OH} = 2.0 J _{3Me} = 0.3
33	2-Hydroxylamino-4,6-dinitro-	8.09	8.25	2.35	J _{NH-OH} = 2.0 J ₂₃ = 2.3

^a The expected multiplicities and integrated intensities are observed for all signals.^b 100.1 MHz, Acetone-d₆ solvent tetramethylsilane reference.^c The NH₂ signals appear as broad singlets (~15 Hz fwhm).

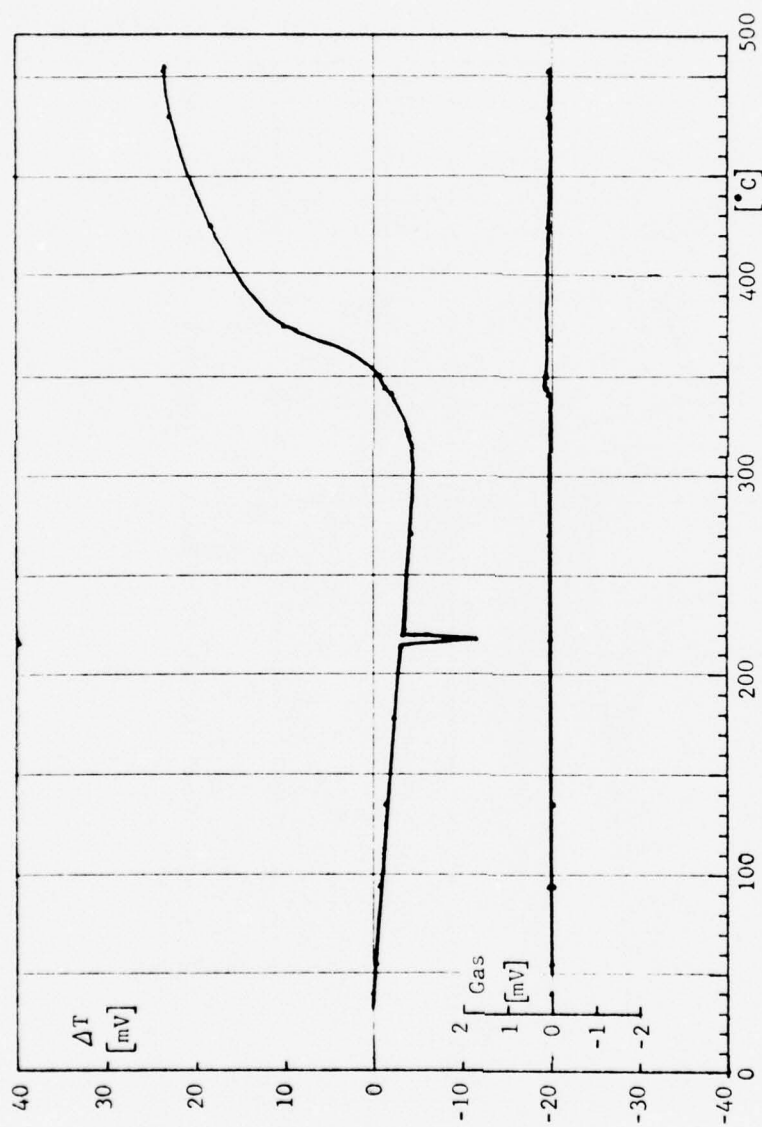


FIGURE 1. Differential Thermal Analysis (DTA), Heating Rate = 10°C/min.
Sample: 3.3 mg 2-amino-3,5-dinitrotoluene (12), m.p. 215 to 217°C.

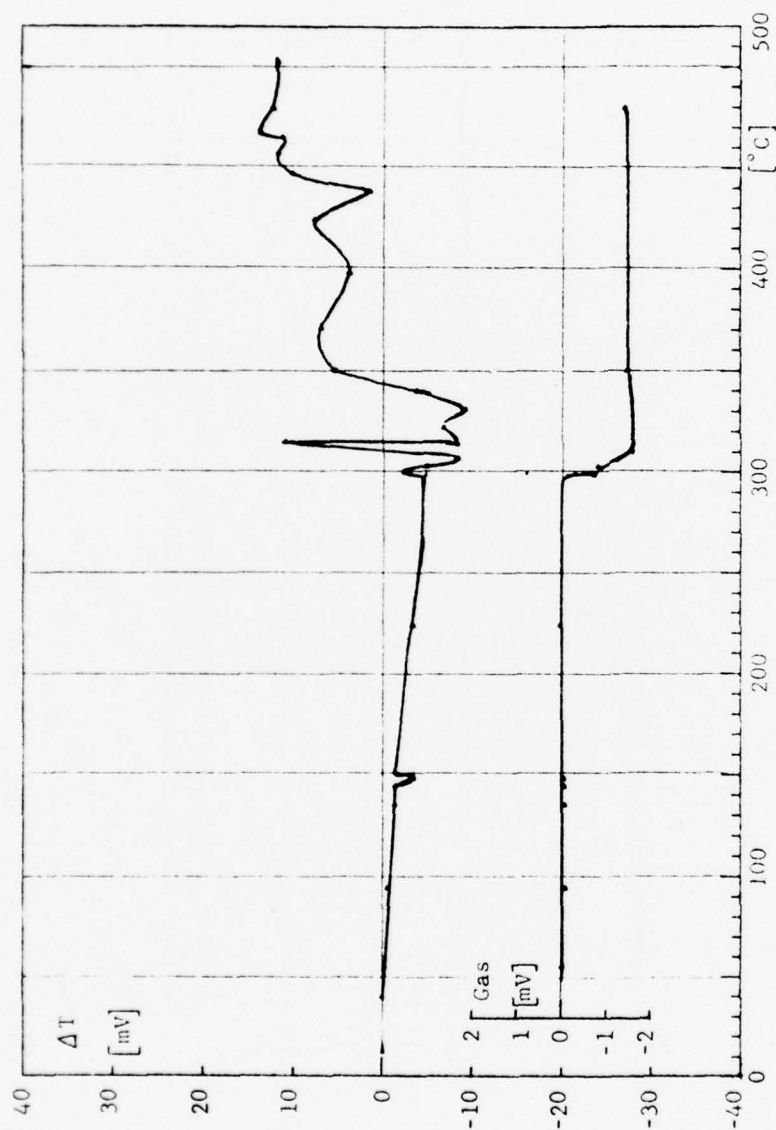


FIGURE 2. DTA, Heating Rate = 10°C/min. Sample: 3 mg 2-amino-3,6-dinitrotoluene (13), m.p. 148 to 151°C.

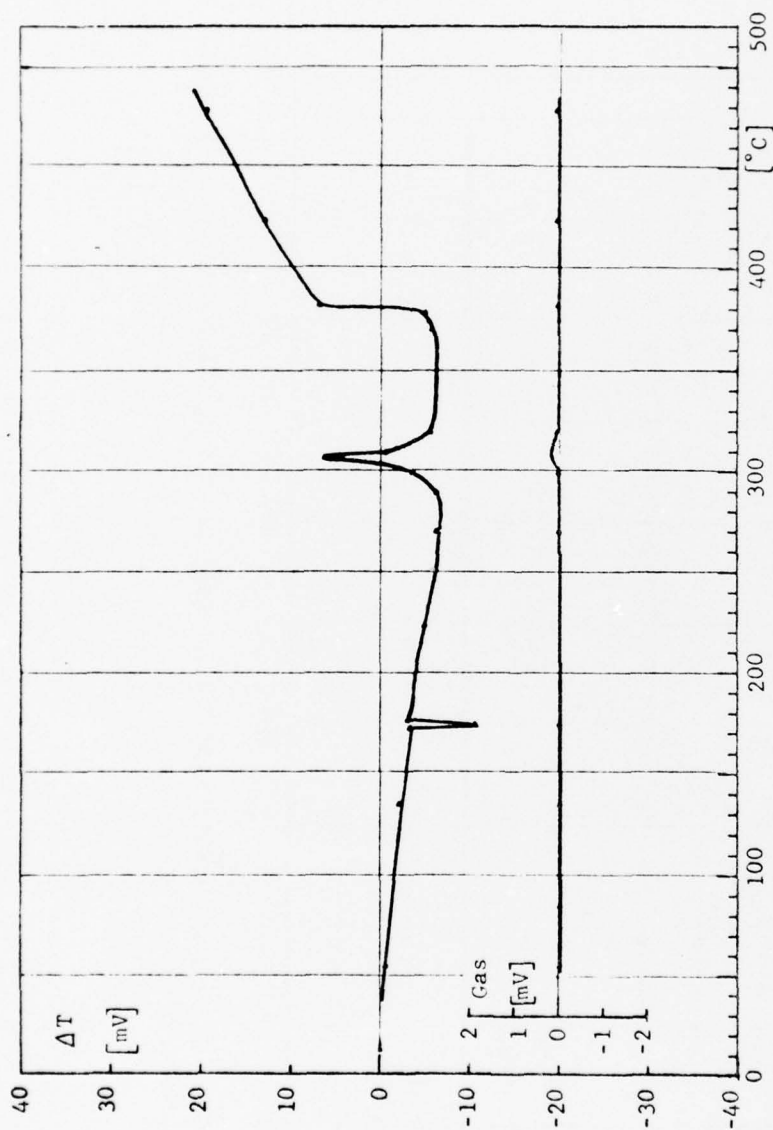


FIGURE 3. DTA, Heating Rate = 10°C/min. Sample: 2.3 mg 2-amino-4,6-dinitrotoluene (15), m.p. 175 to 176°C.

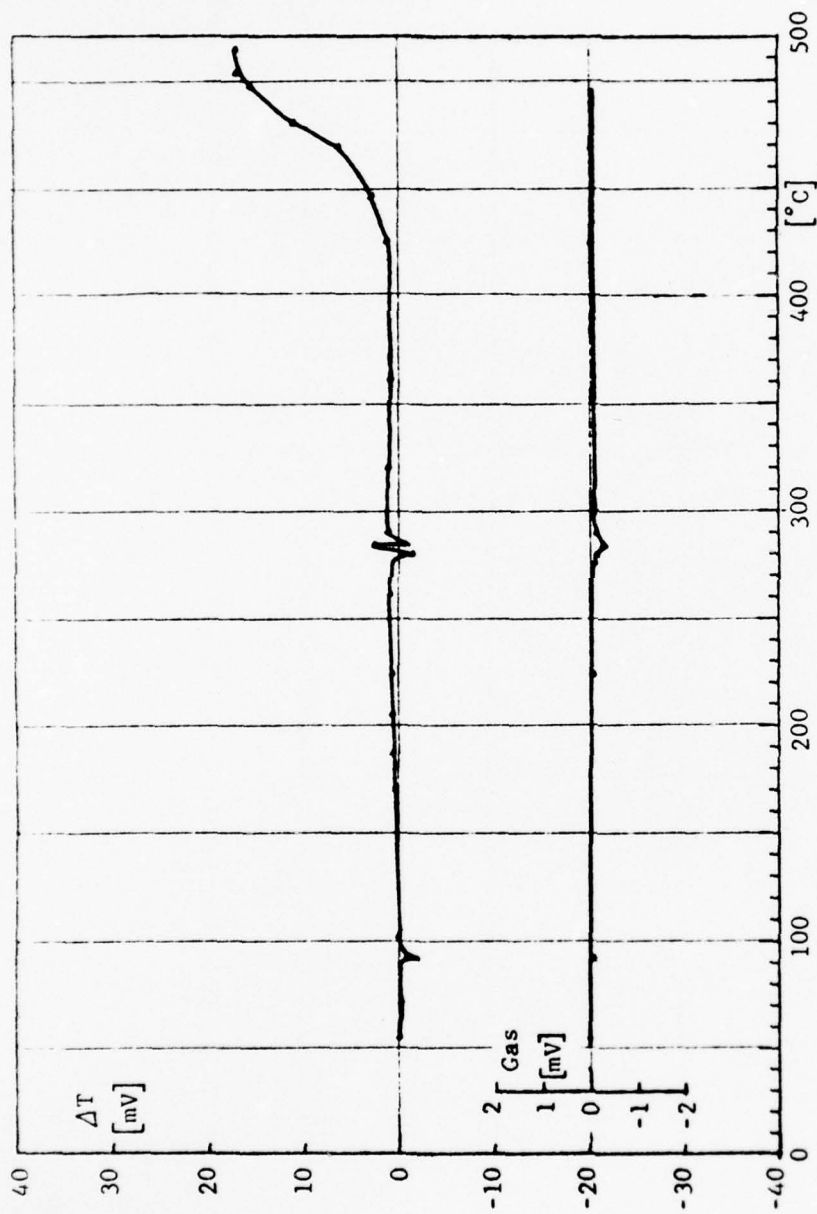


FIGURE 4. DTA, Heating Rate = 10°C/min. Sample: 2.2 mg 3-amino-2,4-dinitrotoluene (17), m.p. 94°C.

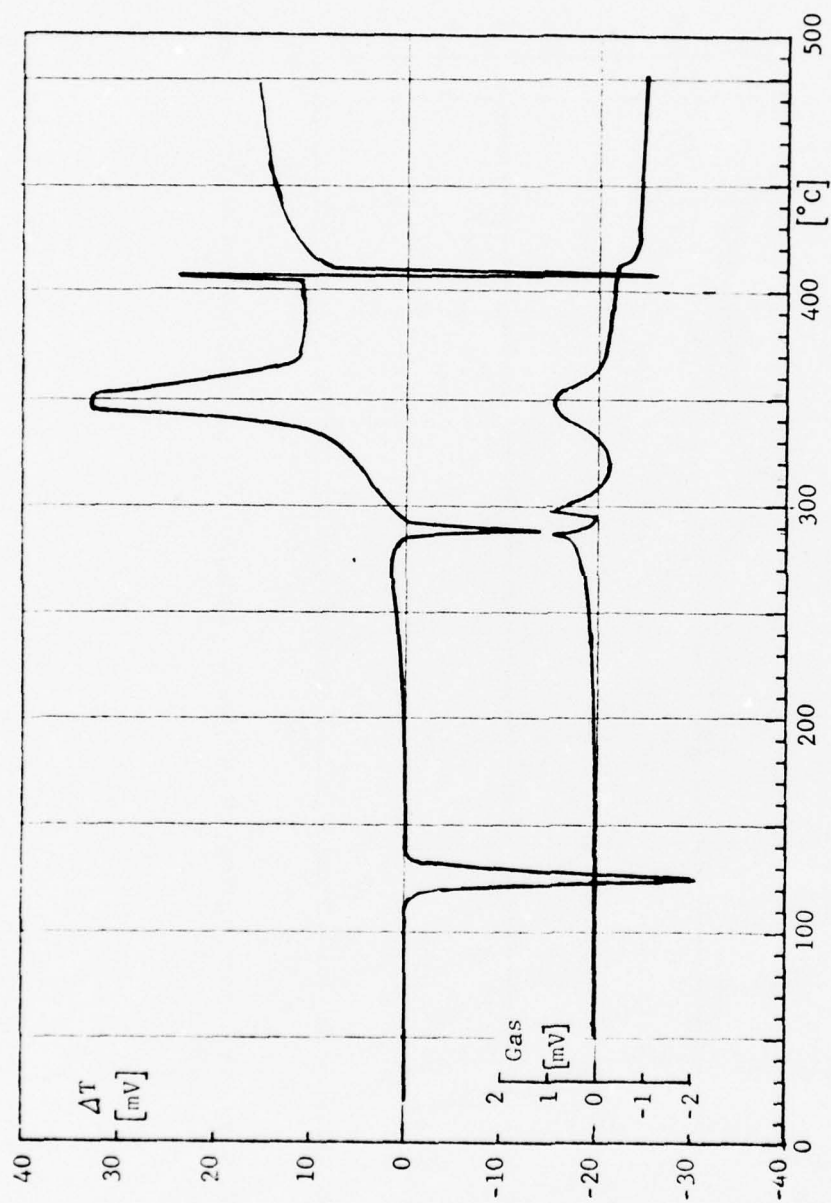


FIGURE 5. DTA, Heating Rate = 10°C/min. Sample: 2.2 mg 3-amino-2,5-dinitrotoluene (18), m.p. 127 to 128°C.

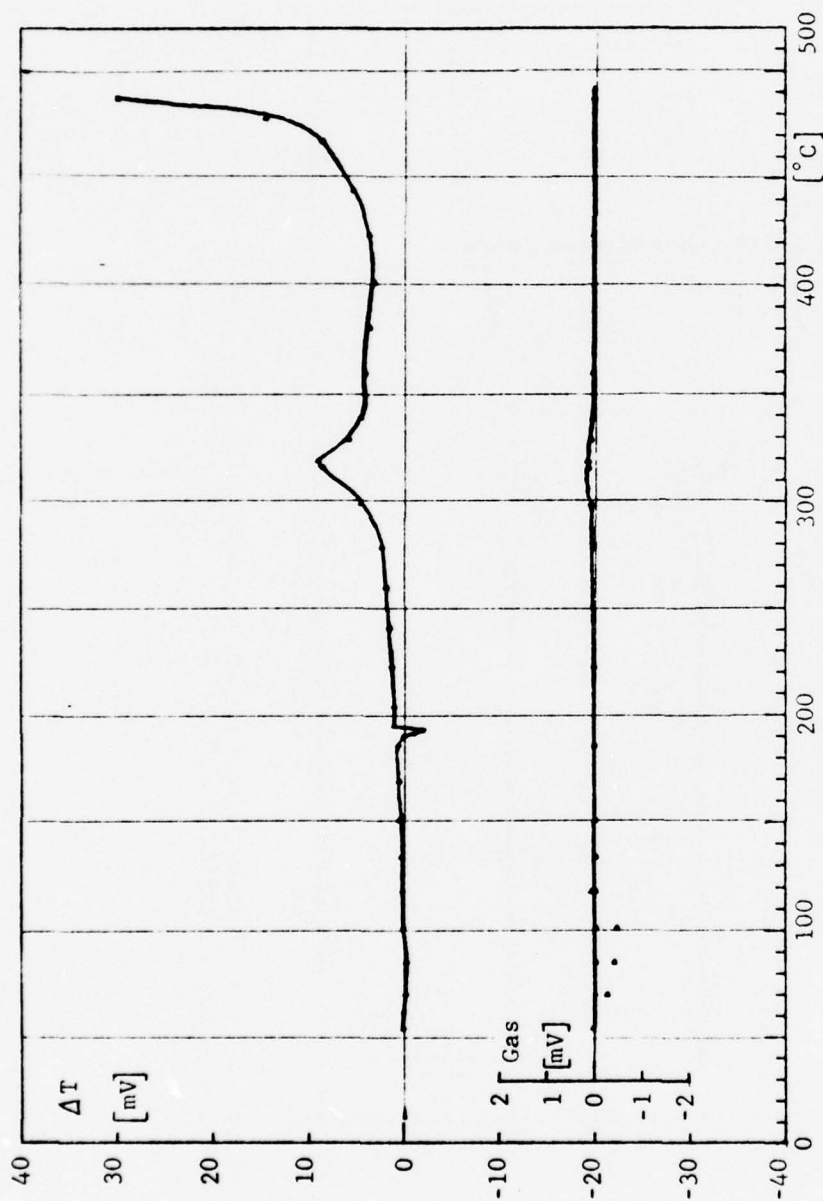


FIGURE 6. DTA, Heating Rate = $10^{\circ}\text{C}/\text{min}$. Sample: 3.1 mg 5-amino-2,4-dinitrotoluene (21), m.p. 197 to 199°C .

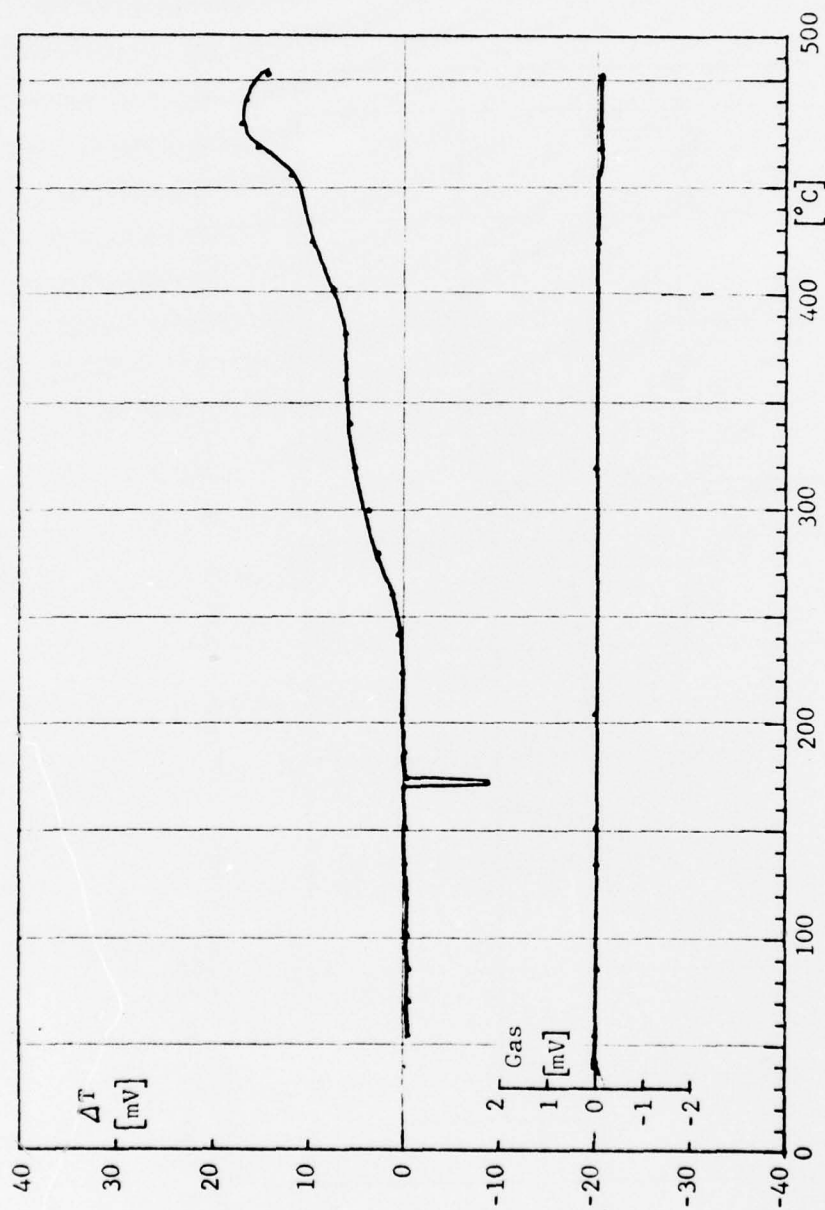


FIGURE 7. DTA, Heating Rate = 10°C/min. Sample: 3.8 mg 4-amino-3,5-dinitrotoluene (23), m.p. 176 to 177°C.

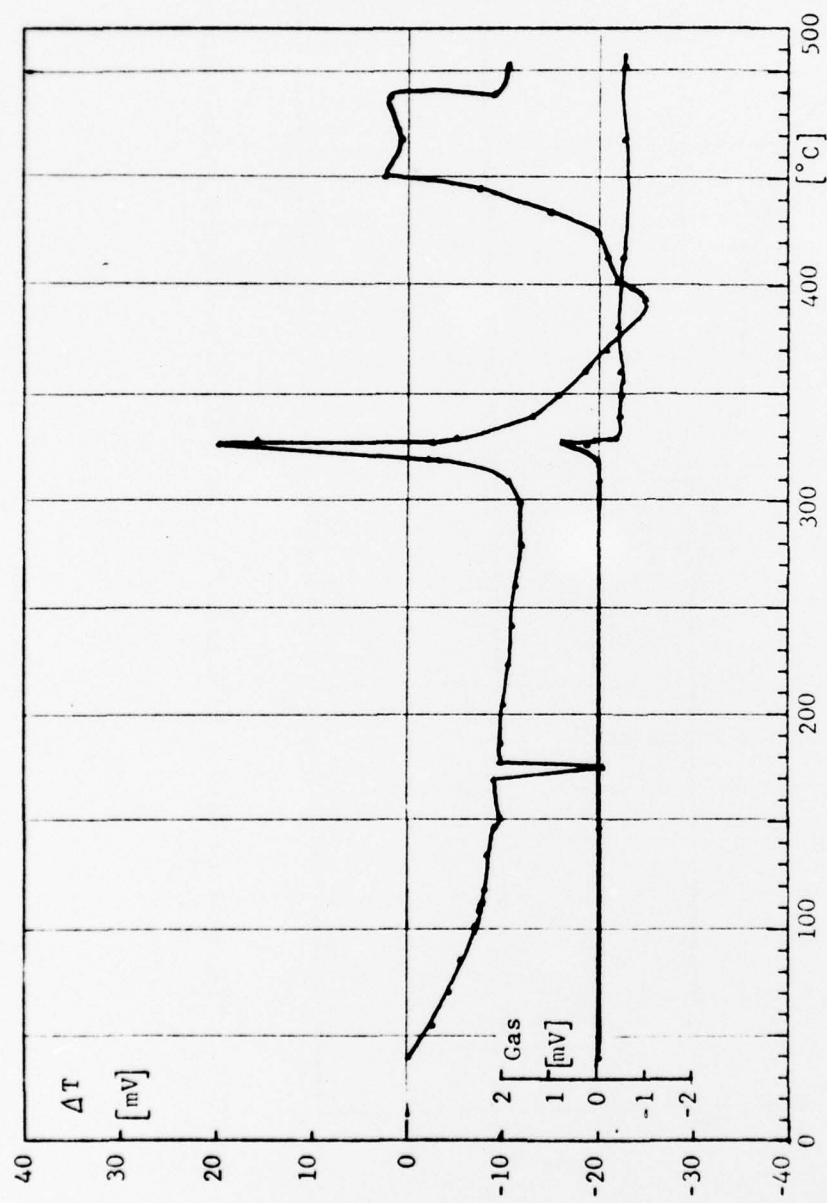


FIGURE 8. DTA, Heating Rate = 10°C/min. Sample: 6.2 mg 4-amino-2,6-dinitrotoluene (25), m.p. 171 to 172°C.

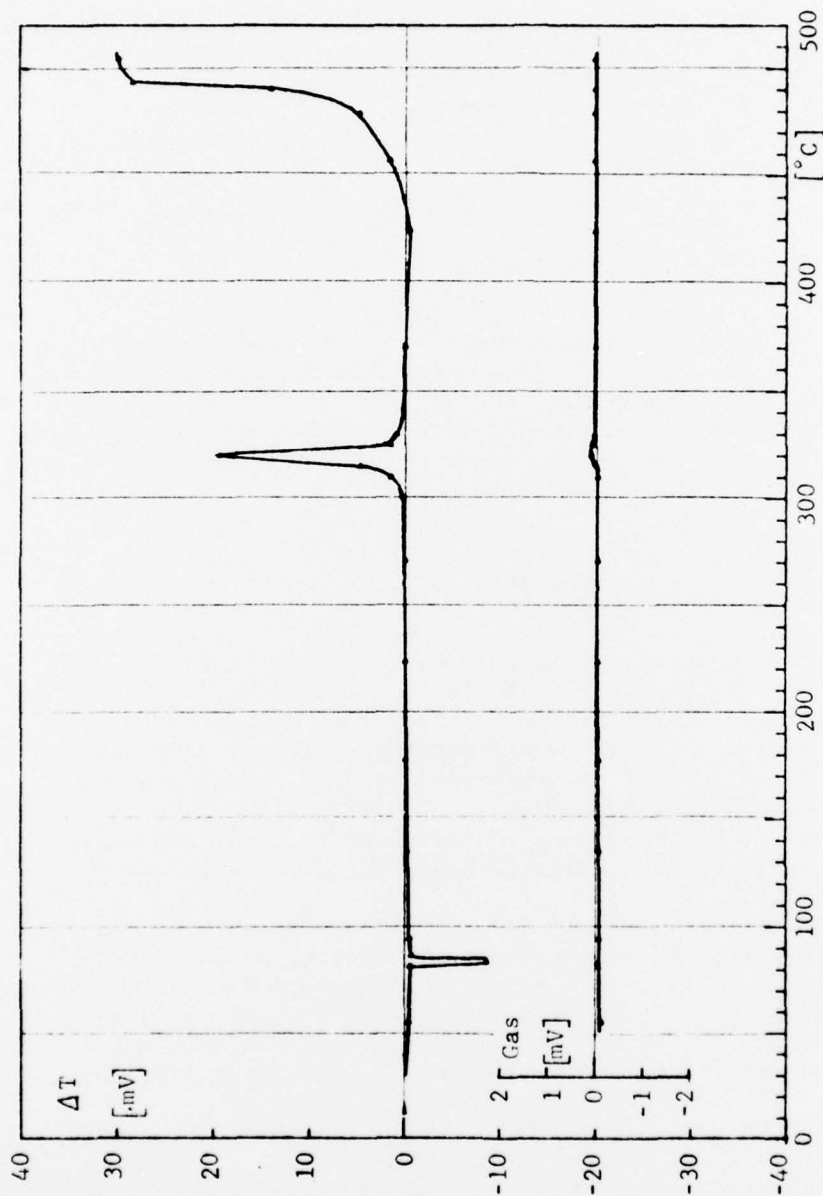


FIGURE 9. DTA, Heating Rate = $10^{\circ}\text{C}/\text{min}$. Sample: 5 mg 2,4,6-trinitrotoluene (α -TNT, 1), m.p. 80.6°C .

greater stability than 17 and 23 and to resemble most closely 12, 13, 15, 19, 21, and 25 in their stability, i.e., decompose near 300 to 325°C.

Measured impact sensitivities of the eight aminodinitrotoluenes (12, 13, 15, 17, 18, 21, 23, and 25) indicate very high stability of these compounds. Values obtained (35 mg samples; 2.5 kg weight) were greater than 180 cm, the limit of the instrument; the reference value for α -TNT was 75 cm. One exception is 4-amino-2,6-dinitrotoluene (25) which has an impact sensitivity of 169 cm.

CONCLUSIONS

It is concluded from the present study that the aminodinitrotoluenes, as a group, are rather stable compounds -- much more stable to impact than α -TNT itself. They are also very stable to heat. Thus, although certain aminodinitrotoluenes could conceivably form by reaction of ammonia with trace amounts of TNT isomers present in crude TNT, these reaction products are not sensitive explosives.

EXPERIMENTAL SECTION

Infrared spectra were determined on a Perkin Elmer Model 137; ^1H NMR spectra were determined on a Varian XL-100 spectrometer with Transform Technology TT-100 pulsed Fourier transform system. Proton and ^{13}C chemical shift measurements were determined at ca. 30°C and are referenced to tetramethylsilane internal standard. Mass spectra were determined on an Hitachi Model RMU-6E. Melting points are corrected. Elemental analyses and molecular weights (vapor osmometry) were determined by Galbraith Laboratories, Knoxville, Tennessee.

Impact sensitivities of all samples were determined as 50% positive values from 25 shots using an impact tester (Bureau of Mines design) equipped with a 2.5 kg weight. Anvils and hammers were made of Ketos oil hardening tool steel, heat treated to Rockwell C-55-60 hardness. The surfaces of the tools were ground. Sample weight per shot was 35 ± 2 mg. Samples were placed on sandpaper, 5/0 grit carborundum.

The hammer surface was cleaned with acetone and wiped dry after each shot to remove residues of previous samples. Freshly ground hammers were used after each 25 shots to ensure constant testing conditions.

Evaluation of the shots was made by visual observation of hammer surface and sample. A shot was considered positive when black reaction spots were formed.

All samples, with one exception, had measured impact sensitivities greater than the limit of the instrument (180 cm); 4-amino-2,6-dinitrotoluene (25) had a value of 169 cm. 2,4,6-Trinitrotoluene (1), a reference compound, produced a value of 75 cm in the tests.

Differential thermal analysis measurements were determined on a Perkin Elmer Model DSC-1B instrument. Samples of 2 to 6 mg were used and temperature curves and gas evolution curves were plotted for aminodinitrotoluenes 12, 13, 15, 17, 18, 21, 23, 25, and α -TNT (reference compound). Heating rate was 10°C/min. Data are plotted in Figures 1 through 9. The plot of Figure 5 was obtained on a modified instrument having different sensitivity settings which accounts for the difference in response magnitude relative to the other figures. Decomposition temperatures are listed in Table 3. Endotherms correspond closely to observed capillary melting points. Initial exothermic maxima (usually sharp, as with α -TNT) are considered decomposition temperatures and are usually accompanied by gas evolution at the same temperature. Neither gas evolution nor a sudden exotherm was observed with 4-amino-3,5-dinitrotoluene (23) (Figure 7); behavior of 2-amino-3,5-dinitrotoluene (12) was similar (Figure 1). An exotherm slowly increasing with temperature was noted with these compounds; decomposition temperatures listed in Table 3 for these materials are measured at the onset of the exotherm and are therefore lower than values reported for the other compounds.

2-Amino-3,6-dinitrotoluene (13) was prepared by treating 2,3,6-trinitrotoluene (η -TNT) with excess ethanolic ammonia and heating under reflux according to the procedure of Körner and Contardi;¹⁶ the product was purified by recrystallization from ethanol, m.p. 148 to 151°C.

3-Amino-2,4-dinitrotoluene (17) was prepared in a manner similar to the preparation of 13 from 2,3,4-trinitrotoluene (β -TNT) by the procedure of Hepp;⁹ the product was purified by recrystallization from aqueous acetic acid (20% water), m.p. 92 to 93°C.

5-Amino-2,4-dinitrotoluene (21) was prepared by treating 2,4,5-trinitrotoluene (γ -TNT) with excess ethanolic ammonia at 25°C according to the procedure of Hepp;⁹ recrystallization from acetic acid gave a purified product, m.p. 197 to 199°C.

4-Amino-3,5-dinitrotoluene (23) was prepared from 3,4,5-trinitrotoluene (δ -TNT) in a manner similar to the preparation of 21; recrystallization from ethanol gave a purified product, m.p. 176 to 177°C.

Reduction of 2,4,6-Trinitrotoluene With Hydrogen Sulfide in Dioxane Solvent. Preparation of 4-amino-2,6-dinitrotoluene (25). 2,4,6-Trinitrotoluene (100 g, 0.44 mole) in 250 ml of dioxane was treated with concentrated ammonium hydroxide (0.5 ml) and hydrogen sulfide bubbled through, keeping the temperature below 40°C until no further exothermic reaction was observed.^{26,44} Sulfur was removed by filtration. The product was isolated as its hydrochloride salt by passing dry hydrogen chloride into the filtrate to yield 38 g (37%) of

25 hydrochloride, m.p. 169 to 171°C (literature m.p. 172°C²⁶). The salt was converted to the free base by treatment with aqueous sodium hydroxide; recrystallization from ethanol gave crystals (80% recovery) m.p. 167 to 168°C (literature m.p. 169°C⁴⁴; 171 to 172°C²⁵; 171°C³⁴). Analysis of the crude 25 by proton NMR indicated a mixture of 4-amino-2,6-dinitrotoluene (25) (99%) and 2-amino-4,6-dinitrotoluene (15) (1%).

Reduction of 2,4,6-Trinitrotoluene with Hydrogen Sulfide in Ethanol Solvent. 2,4,6-Trinitrotoluene (100 g, 0.44 mole) suspended in 500 ml of absolute ethanol containing 0.5 ml of concentrated ammonium hydroxide was treated with a rapid stream of hydrogen sulfide gas for 1 hr, keeping the reaction temperature at 25 to 30°C by ice-bath cooling.^{30,33} The reaction mixture was filtered to remove sulfur and the filtrate was diluted with water (1 liter) to yield 64.8 g of product mixture, m.p. 100 to 120°C. Assay of this mixture by column chromatography on silica (elution with benzene) revealed three principal bands (gravimetric analysis): (1) unreacted TNT (23%); (2) a mixture of 4-amino-2,6-dinitrotoluene (25) and 2-amino-4,6-dinitrotoluene (15) in a ratio of ca. 9:1 by NMR and gas liquid chromatography assay (28% total); and (3) a mixture of 2-hydroxylamino-4,6-dinitrotoluene (33) and 4-hydroxylamino-2,6-dinitrotoluene (32) (49% total). The mixtures of 25 and 15 and of 32 and 33 could not be separated by thin layer or column chromatography on silica or alumina. The assay was established more accurately by proton NMR giving the values: TNT (22%), 25 (22%), 15 (4%), 32 (44%) and 33 (8%); measurements were made in (CD₃)₂CO solvent using both methyl and aryl signals for integration. Spectra of pure components are summarized in Table 5.

4-Hydroxylamino-2,6-dinitrotoluene (32). A 60.0-g aliquot of the above product mixture from reduction of α -TNT with hydrogen sulfide in ethanol was fractionally extracted with refluxing benzene in a Soxhlet extractor. After four single extractions of 500 ml each (which removed most of the 25 and 15), the remaining solid was extracted continuously until all was extracted (1.5 hr). Cooling of the final extract deposited 11.7 g of crystalline product which assayed 90% 32 by thin layer chromatography; recrystallization from benzene gave very pure 32, m.p. 143 to 147°C (literature m.p. 143 to 145°C³⁰); mol. wt. calculated for C₇H₇N₃O₅: 213.15; found (mass spectrometry) 213 (parent peak).

2-[N-(4-toluenesulfonyl)]-5-nitrotoluene (30) was prepared by nitration of 85.6 g (0.328 mole) of 2-[N-(4-toluenesulfonyl)]toluene (29) with 25% nitric acid by the procedure of Platt and Sharp⁴⁰ to yield 98 g (97%) of 30, m.p. 176 to 178°C after recrystallization from ethanol; literature m.p. 174 to 175°C⁴⁰.

3,5-Dinitro-2-[N-(4-toluenesulfonyl)]toluene (31) was prepared by nitration of 49.0 g (0.16 mole) of 2-[N-(4-toluenesulfonyl)]-5-nitrotoluene (30) with 35% nitric acid as described by Platt and Sharp⁴⁰ to yield 52 g (93%) of 31, m.p. 160 to 163°C after recrystallization from ethanol; literature m.p. 161 to 163°C⁴⁰.

2-Amino-3,5-dinitrotoluene (12) was prepared by hydrolysis of 50 g (0.142 mole) of 3,5-dinitro-2-[N-(4-toluenesulfonyl)]toluene (31) with concentrated sulfuric acid at 110°C⁴⁰ to yield 16.6 g (57%) of 12 after recrystallization from ethanol, m.p. 215 to 217°C (literature m.p. 217 to 218°C¹; m.p. 211 to 213°C⁴⁰).

2-Amino-4,6-dinitrotoluene (15). 2-Methyl-3,5-dinitrobenzoic acid (11.3 g, 0.050 mole) was converted to 2-amino-4,6-dinitrotoluene by the Schmidt reaction according to the procedure of Zbarskii *et al.*⁴³ After recrystallization first from ethanol and then from benzene there was obtained 6.0 g (61%) of crystals, m.p. 175 to 177°C (literature m.p. 173 to 174°C; crystallized from methanol²⁵).

o-Methylisonitrosoacetanilide (35) was prepared by the procedure of Cassebaum⁵⁸ from *o*-toluidine (0.50 mole) to yield 61.0 g (69%) of crystalline 35, m.p. 120 to 121°C; Sandmeyer reports m.p. 121°C⁶⁵.

7-Methyl-5-nitroisatin (37) was prepared by the procedure of Cassebaum⁵⁸ from 61 g of *o*-methylisonitrosoacetanilide (35) to yield 56.8 g (81%) of 37 as orange crystals, m.p. 250 to 255°C (decomposition); literature m.p. 248 to 249°C⁵⁶.

2-Amino-3-methyl-5-nitrobenzoic Acid (38) was prepared from 56.8 g of 7-methyl-5-nitroisatin (37) by the procedure of Cassebaum⁵⁸ to yield 51.0 g (96%) of 38 as a yellow powder, m.p. 260 to 263°C (decomposition); literature⁵⁸ m.p. 265 to 268°C (crude), 268°C (crystallized from acetic acid).

2,5-Dinitro-3-methylbenzoic Acid (39). To trifluoroacetic acid (100 ml) in a three-necked flask, chilled in an ice bath (2°C), was added, with stirring, 3.3 ml (0.13 mole) of hydrogen peroxide (98% assay). With continued stirring was added 20.3 ml (0.144 mole) of trifluoroacetic anhydride during 0.5 hr keeping the temperature at 2 to 3°C. To the resulting solution was added 6.53 g (0.033 mole) of 2-amino-3-methyl-5-nitrobenzoic acid (38) during 5 min. A reflux condenser was attached to the flask and the ice bath removed causing the solution to warm spontaneously to 42°C within 20 min. The reaction mixture was then heated under reflux for 3 hr. The deep-orange colored solution was concentrated to dryness under reduced pressure and the residue triturated with 100 ml of water. The insoluble product was removed by filtration, washed with water and dried to yield 5.64 g (75%) of 39, m.p. 170 to 177°C; two recrystallizations from aqueous methanol (90% methanol) gave straw-colored prisms, m.p. 180 to 181°C (61.5% recovery); ir (KBr) 1730 cm⁻¹ (C = O).

Analysis. Calculated for C₈H₆N₂O₆: C, 42.49; H, 2.67; N, 12.39; mol. wt. 226.14. Found: C, 42.68; H, 2.69; N, 12.37; mol. wt. 230 (vapor osmometry, chloroform).

3-Amino-2,5-dinitrotoluene (18). 2,5-Dinitro-3-methylbenzoic acid (39, 2.43 g, 0.0108 mole) was dissolved in 21.5 g of 104% sulfuric acid (20% SO_3 , 80% H_2SO_4). While stirring and keeping the temperature at 5 to 10°C by ice-bath cooling, powdered sodium azide (0.84 g, 0.013 mole) was added cautiously in portions of less than 0.1 g during 1 hr. (CAUTION: If the sodium azide is added too rapidly an explosion may result.) Stirring the mixture was continued at 0 to 10°C for 1 hr (gas evolution occurs), 10 to 30°C for 2 hr, and 30 to 60°C for 3 hr. The dark mixture was then poured onto 200 ml of crushed ice to yield a yellow-orange precipitate which was removed by filtration, washed with water and dried to yield 2.02 g (95%) of 18, m.p. 125 to 127°C; recrystallization from 95% ethanol gave rust-colored flakes, m.p. 127 to 128°C (79% recovery); ir (KBr) 3400, 3250 cm^{-1} (NH).

Analysis. Calculated for $\text{C}_7\text{H}_7\text{N}_3\text{O}_4$: C, 42.64; H, 3.58; N, 21.32; mol. wt. 197.15. Found: C, 42.71; H, 3.62; N, 21.33; mol. wt. 198 (osmometry, chloroform).

2-Diazo-4,6-dinitro-3-methylphenol (40). 2-Methyl-5-nitroaniline (40, 15.2 g, 0.10 mole, m.p. 107 to 109°C) was dissolved in 120 ml of concentrated sulfuric acid with stirring and cooling to 0°C. Fuming nitric acid (90% HNO_3 , $d = 1.5$; 15 ml, 0.32 mole) was added dropwise with stirring during 15 min while maintaining the temperature at 0°C. The reaction mixture was allowed to warm to ambient temperature with continued stirring during 3 hr (possible exothermic reaction since final temperature was 30°C). It was then poured onto 1200 ml of crushed ice and allowed to stand overnight. The gummy, oily product was filtered and triturated with ethanol to yield a dark-orange solid which was crystallized from acetic acid to yield 2.57 g (11.5%) of 42, m.p. 152 to 154°C (vigorous decomposition, followed by an explosion); impact sensitivity (2.5 kg weight) less than 10 cm; ir (Nujol) 2200 ($\text{C} = \text{N}$), 1630 cm^{-1} ; NH bands absent; NMR [$(\text{CD}_3)_2\text{C} = \text{O}$] δ 6.78(s, 1, ring CH), 270(s, 3, CH_3), mol. wt. (mass spectrometry) 224 (parent peak); mol. wt. calculated for $\text{C}_7\text{H}_4\text{N}_4\text{O}_5$: 224.13.

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